



Study On The Adsorption Of Cd^{+2} , Cu^{+2} , Zn^{+2} , Co^{+2} , La^{+3} And Y^{+3} Metal Ions On Titanium Oxide-Cerium Phosphate Nanocomposite Membrane

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ABSTRACT

Sorption is one of the most promising techniques due to its advantages of high efficiency, low operation temperature, and high selectivity. Nanotitanium oxide(TiO_2), nanofibrous cerium phosphate, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}(\text{nCeP}_f)$, and novel sorbents titanium oxide-cerium phosphate nanocomposite membranes, $[\text{nTiO}_2]_{(0.10)}[\text{nCeP}_f]_{(0.90)}$, $[\text{nTiO}_2]_{(0.25)}[\text{nCeP}_f]_{(0.75)}$, were prepared and characterized. Studies the adsorption of divalent metal ions Cd^{+2} , Cu^{+2} , Zn^{+2} , Co^{+2} and La^{+3} , Y^{+3} metal ions on nanofibrous cerium phosphate and on the novel nanocomposite membranes, in nitric acid solution of pH 4, were carried out. The uptake of the divalent metal ions were estimated by atomic absorption spectroscopy, while the uptake of La^{+3} and Y^{+3} metal ions were estimated by complexation method using EDTANa_2 . From the distribution coefficients (K_d values) calculations it was found high selectivity of Cd^{+2} and Zn^{+2} metal ions with $[\text{nTiO}_2]_{(0.25)}[\text{nCeP}_f]_{(0.75)}$ nano composite membrane. High uptake of La^{+3} and Y^{+3} was also found with $[\text{nTiO}_2]_{(0.25)}[\text{nCeP}_f]_{(0.75)}$ nano composite membrane. In general the sorbents used were found to be very efficient without suffering any extensive decomposition.

Keywords: Titanium oxide; fibrous cerium phosphate; titanium oxide-cerium phosphate nanocomposite membranes; adsorption of divalent and; La^{+3} , Y^{+3} metal ions.

1. Introduction

Tetravalent metal phosphates are very insoluble compounds with good thermal stabilities and high ion exchange capacities[1,2]. The discovery of their crystalline materials [3,4], represent a fundamental step in chemistry of these compounds with general

formula $\alpha\text{-M(IV)(HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\gamma\text{-M(IV)PO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, (where $\text{M} = \text{Ti, Zr, Hf, Ge, Sn and Ce}$). These materials contain structural POH groups with labile protons. They can exchange their protons with counter ions such as alkali, alkaline earth, transition divalent and trivalent metal ions

[1-4] and act as intercalates [1,2,5,6]. Increase attention direct toward their intercalation [5,6], catalytic[7], electrical conductance[8], and sensors[9]. Layered zirconium phosphates have potential applications as inorganic fillers, sorbents and solid acid catalysts [7, 10-16].

A number of organic membranes are available today. However, very little studies were carried out on inorganic membranes of tetravalent metals. Membranes consist of inorganic polymers such as membrane of MIV phosphates are very attractive and suitable for many processes of chemical technology such as waste disposal of metal ions, intercalates electrical conductance and solid acid catalysts.

$\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and pellicular hafnium phosphate, $\text{Hf}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and their γ -types were reported[17-19]. The pellicular membranes are two dimensional (2-D) structure membranes.

Transition metal oxides composed of oxygen atoms bound to transition metals. They are commonly utilized for their catalytic activity and semi conductive properties. They also frequently used as pigments in paints and plastics, most notably titanium dioxide. Transition metal oxides have a wide variety of surface structures which affect the surface energy of these compounds and influence their chemical properties [20-22].

Most transition metals have more than one oxidation state. Wide varieties of nanostructures for metal oxides are reported in open literature. Nanosized oxides (e.g., TiO_2 , ZrO_2 , SnO_2 , NiO , CeO_2 , Nb_2O_5 , Fe_2O_3 , Co_3O_4) have been heavily investigated [21-22].

TiO_2 has exhibited photo activity toward degradation of dye and other organic compounds [23-25].

Titanium dioxide also known as titanium(IV) oxide with the chemical formula TiO_2 , is a white, water-insoluble solid. It is versatile material of photo catalytic properties, low cost, good biocompatibility, and high chemical stability, titanium dioxide, especially at the nanometer scale, have been investigated extensively and intensively in applications from energy and environment to health. Various factors, such as shapes, size, and special facets, will have significant influence on the properties of TiO_2 nanomaterials. For that reason a variety of synthesis methods have been developed to fabricate TiO_2 nanomaterials with different

morphologies and textures. TiO_2 nanomaterials with well-controlled shape (e.g., nanorod, nanowire, and nanotubes) and desired properties [26-28].

Hydrated titanium dioxide shows to have ion-exchange selectivity of a number of divalent metal ions and cesium cations[29].

Recently TiO_2 has greatly extended its applications in many other areas, such as sensors [30] lithium-ion batteries and super capacitors [31] and environment remediation [32].

Fibrous cerium phosphate and its composites were reported recently[33,34].

2. Experimental

2.1. Chemicals

$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, H_3PO_4 (85%) of BDH, TiCl_4 of Reidel De-Haen. Other reagent used were of analytical grade, 0.05 M of each Co^{+2} , Cu^{+2} , Zn^{+2} and Cd^{+2} 0.03 M of La^{+3} and Y^{+3} metal salts HNO_3 solution of pH4 were prepared and estimated by atomic absorption spectrometer.

2.2. Equipments for analysis

1. X-ray powder diffractometry Siemens D-500, using Ni-filtered $\text{CuK}\alpha$ ($= 1.54056\text{\AA}$), Philips PW1800, using Ni-filtered $\text{CuK}\alpha$ ($= 1.54060\text{\AA}$).
2. TG/DTA SII Extra 6000 Thermogram, Thermogram C-MOM. Budapest TGA, Perkin Elmer thermo gravimetric analyzer (TGA) US.
3. Scanning electron microscopy (SEM) Jeol SMJ Sm 5610LV.
4. Transmission electron microscopy Zeiss TEM 10 CR.
5. Fourier Transform IR spectrometer, model IFS25 Bruker 25, FT/IR-6100, Cary630 FT-IR.
6. PH Meter GW521.

2.3. Preparation of nano fibrous cerium phosphate, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$

Nanofibrous cerium phosphate membrane (nCeP_f) was prepared by adding 300 ml of 0.05 M $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$ in 0.5 M H_2SO_4 solution, drop wise, to 300 ml of 6 M H_3PO_4 at $\sim 80^\circ\text{C}$, with stirring. After complete the addition the resultant material left to digest at that temperature for 4 h. To that mixture 3

liters of hot distilled water (~60 °C) was added with stirring for 1 h. The resulting slurry aqueous solution of fibrous cerium phosphate was kept for further use.

Fibrous cerium phosphate membrane was prepared by filtering on Buchner funnel of 1000 ml of its slurry aqueous solution previously subjected to washing by addition and decantation of distilled water up to pH 3.

2.4. Preparation of nano titanium dioxide (nTiO₂)

TiO₂ nanostructures were prepared by sol-gel technique using 10 ml titanium tetrachloride (TiCl₄), In absolute ethanol (EtOH) and distilled water where water/ alcohol is (50:50). The reaction was performed at room temperature with stirring under a fume hood due to the large amount of chlorine (Cl₂) and hydrochloric acid HCl gases evolved in this reaction. The resulted yellow solution was sonicated in Ultrasonic bath for about three hours. The suspensions obtained were dried in an oven for several hours at 50 °C until amorphous and dried TiO₂ particles were obtained. The obtained powder samples were calcined for one hour in a box furnace at temperature ranging at 500 °C in an ambient atmosphere.

2.5. Preparation of [nTiO₂]_(0.10) [nCeP_f]_(0.90) nanocomposite membrane

0.076 g of nTiO₂ was dispersed into 200 ml slurry aqueous solutions of fibrous cerium phosphate, (nCeP_f content = 0.68 g), at 45 °C, with stirring for 3 h. The resultant product was filtered in Buchner funnel, washed with distilled water and left to dry in air.

2.6. Preparation of [nTiO₂]_(0.25) [nCeP_f]_(0.75) nanocomposite membrane

0.227 g of nTiO₂ was dispersed into 200 ml slurry aqueous solutions of fibrous cerium phosphate, (nCeP_f content = 0.68 g), at 45 °C, with stirring for 3 h. The resultant product was filtered in Buchner funnel, washed with distilled water and left to dry in air.

2.7. Preparation of buffer solution of pH = 5.5 [35]

27.2 g sodium acetate were dissolved in 30 ml distilled water at 35 °C, the solution was cooled to about 25 °C, then 5ml glacial acetic acid was

added with stirring for 10 minutes, the resultant solution was diluted with distilled water up to volume equal 100 ml.

2.8. Equilibration experiments of Co⁺², Cu⁺², Zn⁺² and Cd⁺² metal ions with nCeP_f membrane

To 0.1 g of nCeP_f membrane, a mixture of 5ml of 0.05 M of each divalent metal salts in HNO₃ pH 4 solution was added and equilibrated for 24 h with shaking. The solution was decanted and diluted with distilled water to total volume 100 ml.

2.9. Equilibration experiments of Co⁺², Cu⁺², Zn⁺² and Cd⁺² metal ions with [nTiO₂]_(0.10)[nCeP_f]_(0.90) nanocomposite membrane

To 0.1 g of [nTiO₂]_(0.10)[nCeP_f]_(0.90) nanocomposite membrane a mixture of 5ml of 0.05 M of each divalent metal salts in HNO₃ solution of pH 4 was added and equilibrated for 24 h, with shaking. The solution was filtered, the filtrate was diluted with distilled water to total volume 100 ml.

2.10. Equilibration experiments of Co⁺², Cu⁺², Zn⁺² and Cd⁺² metal ions with [nTiO₂]_(0.25)[nCeP_f]_(0.75) nanocomposite membrane

To 0.1 g of [nTiO₂]_(0.25)[nCeP_f]_(0.75) nanocomposite membrane a mixture of 5 ml of 0.05 M of each divalent metal salts in HNO₃ solution of pH 4, was added and equilibrated for 24 h, with shaking. The solution was filtered, the filtrate was diluted with distilled water to total volume 100 ml.

2.11. Equilibration experiments of La⁺³ and Y⁺³ nCeP_f membrane

To 0.1 g of nCeP_f membrane 5 ml of 0.03 M of each trivalent metal salts La⁺³ and Y⁺³ in HNO₃ solution of pH 4 and equilibrated for 24 h, with shaking. The solution was filtered, the filtrate was diluted with distilled water to total volume 100 ml.

2.12. Equilibration experiments of La⁺³ and Y⁺³ with [nTiO₂]_(0.10)[nCeP_f]_(0.90) nanocomposite membrane

To 0.1 g of $[\text{nTiO}_2]_{(0.10)}[\text{nCePf}]_{(0.90)}$ nanocomposite membrane, 5 ml of 0.03 M of each metal salts La^{+3} and Y^{+3} in HNO_3 solution of pH 4 was equilibrated for 24 h, with shaking. The solution was filtered and diluted to total volume 100 ml.

2.13. Equilibration experiments of La^{+3} and Y^{+3} with $[\text{nTiO}_2]_{(0.25)}[\text{nCePf}]_{(0.75)}$ nanocomposite membrane

To 0.1 g of $[\text{nTiO}_2]_{(0.25)}[\text{nCePf}]_{(0.75)}$ nanocomposite membrane, 5 ml of 0.03 M of each metal salts La^{+3} and Y^{+3} in HNO_3 solution of pH 4 was equilibrated for 24 h, with shaking. The solution was filtered and diluted to total volume 100 ml.

2.14. Exchange capacities determination [36]

Exchange capacity of nanosized cerium phosphate, $[\text{nTiO}_2]_{(0.10)}[\text{nCePf}]_{(0.90)}$ and $[\text{nTiO}_2]_{(0.25)}[\text{nCePf}]_{(0.75)}$ nanocomposite membrane were determined by addition of 25 ml of 0.1 M NaCl solution to 100 mg of each, with stirring for one h, then titrated with 0.1 M NaOH solution.

2.15. Thermal analysis [36]

Thermal analyses were carried out at temperature range about 20 ~775 °C in nitrogen atmosphere, the rate was 10 °C/min.

The water of hydration of $[\text{nTiO}_2]_{(0.10)}[\text{nCePf}]_{(0.90)}$ and $[\text{nTiO}_2]_{(0.25)}[\text{nCePf}]_{(0.75)}$ nanocomposite membranes, were estimated by heating 0.2 g of each composite in oven at 150 °C for 1.5 h.

3. Results and Discussion

Nanofibrous cerium phosphate $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ (nCePf), and nano titanium oxide (nTiO_2), were prepared and characterized by XRD, FT-IR spectra and SEM.

3.1. XRD of nCePf

Nanosized fibrous cerium phosphate, was obtained via reflux method. The fibrous nature can be visually recognized. Its XRD of is shown in Figure 1, with $d_{001} = 10.89 \text{ \AA}$.

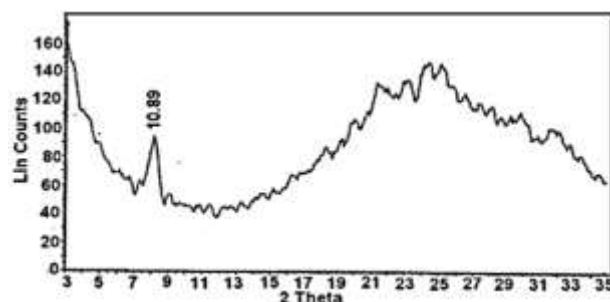


Fig. 1. XRD of nanofibrous cerium phosphate

3.2. TGA

Thermogram of $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ is shown in Figure 2. The thermal decomposition occurs in continuous process almost one step. The thermal analysis was carried out at temperatures between 10-775 °C, the final product was CeP_2O_7 , results from the loss of water of hydration between 60-200 °C, followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

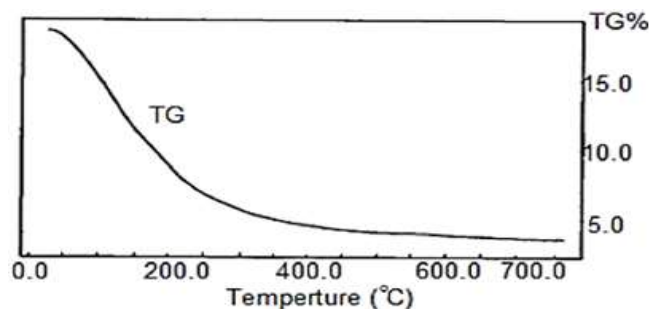


Fig. 2. TGA of nanofibrous cerium phosphate

3.3. FT-IR

Figure 3 shows FT-IR spectrum of nanofibrous cerium phosphate, with a trend similar to that of M(IV) phosphates. It consists of broad band centered at 3350 cm^{-1} is due to OH groups symmetric stretching of H_2O , small sharp band at 1628 cm^{-1} is related to H-O-H bending. Sharp broad band centered at 1045 cm^{-1} is corresponds to phosphate groups vibration. The bands at the region $630\text{--}450 \text{ cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$.

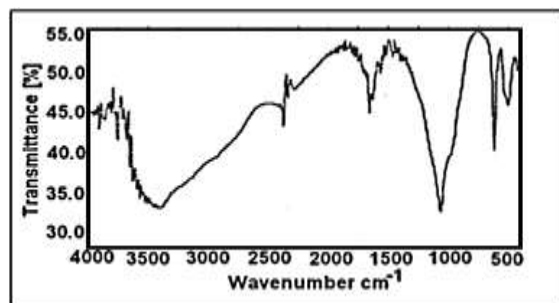


Fig. 3. FT-IR spectra of nanofibrous cerium phosphate

3.4. SEM

SEM morphology image of the nanosized fibrous cerium phosphate shown in Figure 4. The photograph shows its average size is ~20.5 nm.

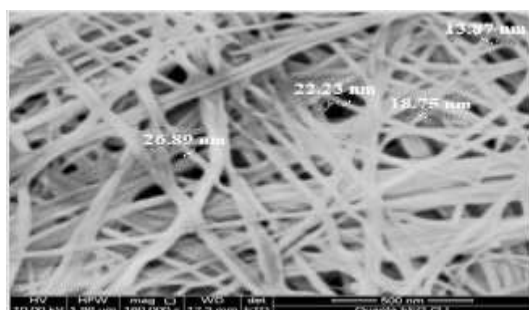


Fig. 4. SEM morphology image nanofibrous cerium phosphate

3.5. TEM

Transmission electron microscopy image (TEM) of the nanosized fibrous cerium phosphate, of fibrous visual look, is shown in Figure 5. The photograph shows its average size is ~15 nm. The TEM were performed from PVA/nCeP_f composite in mixing ratios 9:1, respectively. That used to provide for 1st time the clear texture of nCeP_f. The fibrous morphology was quite evidence, shows the stacking of these fibers. That was observed for typical TEM fibrous textures. Generally, fibrous morphology usually has hollow nature

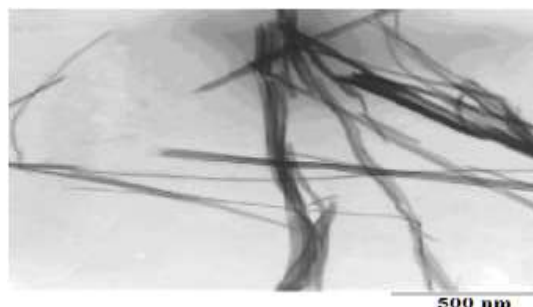


Fig. 5. TEM morphology image nanofibrous cerium phosphate

3.6. XRD of nTiO₂

XRD of nanosized titanium dioxide is shown in figure 6. The synthesized TiO₂ nanoparticles were subjected to powder X-Ray diffraction analysis affirms the presence of TiO₂ nanoparticles. the peaks obtained in the pattern coincides well with the literature[37]. The intensity of the peak is high. The sharpness of the peaks show the sample possess a good crystalline nature. Its nanosized was 70 nm, That were calculated from XRD , using Scherer's equation[38].

$$D = \frac{0.9\lambda}{B2\theta \cos\theta \max}$$

Where **D** is the average crystal size in nm, λ is the characteristic wave length of X-ray used ($\lambda = 1.54056 \text{ \AA}$), θ is the diffraction angle and the **B2 θ** is the angular width in the radius at intensity equal to half of the maximum peak intensity.

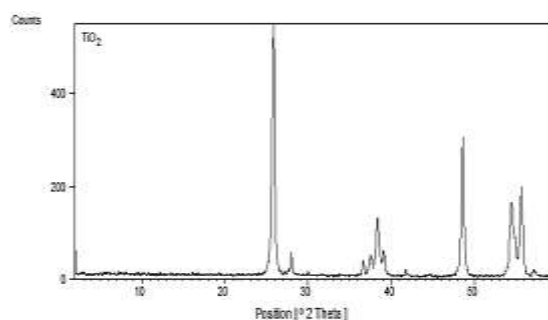


Fig. 6. XRD of nano titanium dioxide

3.7. FT-IR of nTiO₂

Figure 7 represent the FT-IR spectra of nTiO₂, found to be almost in agreement with that reported in literature [28,29].

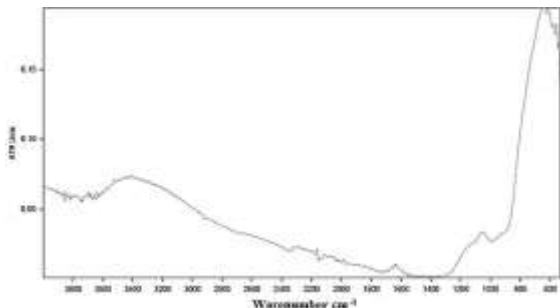


Fig. 7. FT-IR of nano titanium dioxide

3.8. SEM of nTiO₂

SEM morphology image of the nanosized titanium oxide shown in Figure 8. The photograph shows its average size is ~70 nm.

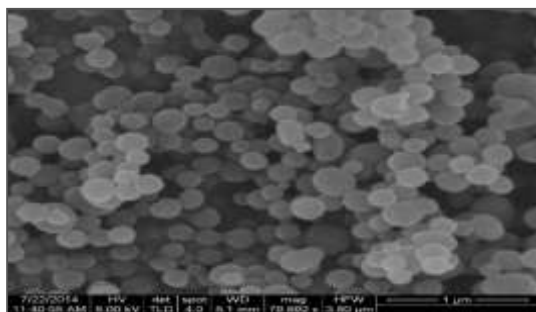


Fig. 8. SEM morphology image of nano titanium dioxide

Ion exchange capacities of nCeP_f, [nTiO₂]_(0.10)[nCeP_f]_(0.90) and [nTiO₂]_(0.25)[nCeP_f]_(0.75) nano composite membranes, were 5.34, 5.80 and 6.65 Meq/g, respectively.

Nano composite membranes of [nTiO₂]_(0.10)[nCeP_f]_(0.90). nH₂O and [nTiO₂]_(0.25)[nCeP_f]_(0.75).nH₂O (n = 2.2-2.5), were prepared by mixing 0.10 : 0.90 and 0.25 : 0.75 wt/wt percentage ratios, respectively. Their water of hydration were thermally determined., accordingly were formulated.

Divalent Co⁺², Cu⁺², Zn⁺² and Cd⁺² metal ions contents in all the equilibrated mixed solutions and their original solutions of mixed 0.05M of metal ions

were determined by atomic absorption spectroscopy. Data is given in Tables 1-4.

Their distribution coefficient of each metal ions were calculated using the following equation:

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M}$$

Where C₀= conc. of original solution of metal ions., C = conc. of equilibrated solution of metal ions, V= volume (ml of metal ions used) . and M= mass of the resin (in grams).

Table 1. standard concentration of Cu⁺² metal ions of 5 ml, C₀= 31775 ppm

Materials	C ppm	Uptake C ₀ -C	K _d
nCeP _f	125.87	662	13.15
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	124.03	698.4	14.08
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	128.23	614.8	11.98

Table 2. standard concentration of Co⁺² metal ions in 5 ml, the C₀= 2945 ppm

materials	C	Uptake C ₀ -C	K _d
nCeP _f	124.52	454.6	9.12
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	125.06	443.8	8.87
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	120.31	538.8	11.20

Table 3. standard concentration of Zn⁺²metal ions in 5 ml, the C₀= 3269 ppm

Materials	C	Uptake C ₀ -C	K _d
nCeP _f	112.84	959.4	21.32
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	102.97	767.8	15.30
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	116.83	932.4	125.27

Table 4: standard concentration of Cd⁺² metal ions in 5 ml, the C₀= 5620 ppm

Materials	C	Uptake C ₀ -C	K _d
nCeP _f	196.26	1694.8	2.16
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	205.46	1510.08	18.37
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	204.84	1523.2	134.44

From tables 1-4 ,the selectivity order (K_d values) for divalent metal ions in ion exchangers were :

nCeP_f Zn⁺² (21.32) > Cu⁺² (13.15) Co⁺² (9.116) > Cd⁺² (2.16)

[nTiO₂]_(0.10)[nCeP_f]_(0.90) Cd⁺² (18.37) > Zn⁺² (15.30) > Cu⁺²(14.08) > Co⁺² (8.87)

[nTiO₂]_(0.25)[nCeP_f]_(0.75) Cd⁺²(134.44) > Zn⁺² (125.27) > Cu⁺² (11.98) > Co⁺² (11.20)

Trivalent La⁺³ and Y⁺³ metal ions contents in all the equilibrated and their original solutions were determined from the analysis of the original metal ions concentration (C₀)and on their non equilibrated solution (C) by complexation method using EDTANa₂. Data is given in Tables 5, 6.

Table 5. standard concentration of La⁺³ metal ions in 5 ml C₀= 1527.09 ppm

Materials	C	Uptake C ₀ -C	K _d
nCeP _f	500.04	986.19	91.02
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	486.15	1041.75	107.14
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	319.47	1208.19	189.12

Table 6. standard concentration of Y⁺³ metal ions in 5 ml C₀= 746.7 ppm

Materials	C	Uptake C ₀ -C	K _d
nCePnCeP _f	118.24	628.46	265.76
[nTiO ₂] _(0.10) [nCeP _f] _(0.90)	222.25	525.45	117.9
[nTiO ₂] _(0.25) [nCeP _f] _(0.75)	168.9	577.8	171.04

From Table 5 ,the selectivity order (K_d values) for trivalent metal ions shows the highest uptake for La⁺³ metal ions was 189.12.

From Table 6 , the selectivity order (K_d values) for trivalent metal ions shows the highest uptake for Y⁺³ metal ions was 265.76.

4 .Conclusion

Thermally stable nanofibrous cerium phosphate, Ce(HPO₄)₂.2.9H₂O(nCeP_f) cation exchanger and nano titanium oxide(TiO₂) ,[nTiO₂]_(0.10)[nCeP_f]_(0.90) and novel [nTiO₂]_(0.25)[nCeP_f]_(0.75) nano composites were prepared and characterized. These materials have potential candidate for the removal of divalent metal ions, Co⁺², Cu⁺², Zn⁺² and Cd⁺² and trivalent metal ions La⁺³ and Y⁺³. Thus these new inorganic ion exchangers are promising for environmental application dealing with heavy metal ions.

The ionic bonding of metal ions in these resins is following sequences of their selectivity order(K_d values), Tables 1-6.

From the distribution coefficient (K_d values) calculations it was found high selectivity of Cd⁺² and Zn⁺² metal ions with [nTiO₂]_(0.25)[nCeP_f]_(0.75) nano composite membrane . High uptake of La⁺³ and Y⁺³ was also found with [nTiO₂]_(0.25)[nCeP_f]_(0.75) nano composite membrane. In general the sorbents used were found to be very efficient without suffering any extensive decomposition.

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